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Moses T. Kabomo

Frank D. Blum

Missouri University of Science and Technology

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Moses T. Kabomo and Frank D. Blum

Department of Chemistry and Materials Research Center
University of Missouri-Rolla
Rolla, MO 65409-0010

Introduction

In the last decade there has been an increased interest in the study of the properties of supported thin polymer films. This has been prompted by the incorporation of thin films into device applications[1] and many other technologies. Although not without controversy, a large body of experimental work indicates departures from bulk behavior by thin films.[2] Strong evidence from both theoretical and experimental work shows that the interaction of polymer with a substrate alters the polymer conformation and mobility. A variety of techniques has been employed to probe the mobility of thin supported polymer films. Some of these techniques indirectly measured chain mobility by inference from the glass transition temperature, T_g.[2]

We report here the results of the study of the glass transition behavior of PMMA thin films supported on silica. By varying the adsorbed amount of PMMA samples of different molecular weights we are able to simultaneously test the effect of molecular weight and adsorbed amount on the T_g. The use of modulated differential scanning calorimetry (MDSC) allows us to probe these very thin films.

Experimental Section

Materials. Two predominantly syndiotactic poly(methyl methacrylate) (PMMA) of narrow polydispersities, purchased from Polymer Source, Inc., were used without further purification. These are denoted as; P88-MMA (M_w = 1.93 x 10^4, M_n/M_w = 1.06) and P792-MMA (M_w = 2.16 x 10^5, M_n/M_w = 1.05). Amorphous fumed silica (Cab-O-Sil M-5, Cabot Corp.), with a manufacturer specified surface area of 200 m^2/g, was dried overnight at 600°C and stored in a dessicator before use. Toluene (analytical grade, Aldrich Corp.) was used as obtained.

Adsorption. 10 mL PMMA solutions of concentrations 5 mg/mL and 15 mg/mL were prepared for each polymer sample. Adsorption was obtained by agitating 20 mL capped glass tubes containing 300 mg of silica and the 10 mL polymer solution at room temperature for 48 hours. The resulting suspension was centrifuged and the concentration of unabsorbed polymer remaining in the supernatant was determined by gravimetric analysis. The polymer-silica gel was dried for 3 days at room temperature and then placed in vacuum at 70 °C for 24 hours.

Characterization. A TA Instrument 2920 DSC was used to measure the glass transition behavior of the bulk and silica adsorbed PMMA samples. Sample masses of about 8 - 12mg were used. Silica was used as the reference. Two heating scans and one cooling scan were taken from 25 °C to 280°C, at a rate of 2.5°C/min and a modulation amplitude of 1°C every 60 s. The sample cell was purged with N_2 gas at a flow rate of 50ml/min during the scans. The first scan ensured that all samples were subjected to similar sample histories and the reported glass transition temperatures are based on the second scan.

Table 1. Polymer Samples of Poly(methyl methacrylate)

Sample	M_w (kg/mol)	M_n/M_w	Bulk T_g (°C)
P88-MMA	19.3	1.06	116
P792-MMA	216	1.05	133

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Results and Discussion

The MDSC curves for the PMMA samples in bulk are shown in **Figure 1**. The T_g is taken as the maximum of the peak of the derivative of the reversing heat flow with respect to temperature, dCp/dT, versus T. For conventional DSC measurements, the T_g is usually taken as the point of inflection of the transition step from the differential heat flow signal, dH/dT or Cp. By taking the derivative of the heat flow signal it becomes easier to distinguish transitions that occur only a few degrees apart. Sharper transitions, like those for bulk polymers, appear as strong peaks on the derivative curve. It has been shown that the T_g of a polymer increases with molecular weight towards an asymptotic limit as expressed by the Fox equation.[3] This molecular weight dependence of the T_g is evident in our results.

The MDSC curves for the PMMA samples adsorbed on silica are shown in **Figure 2** for the adsorbed amounts 0.8 and 1.8 mg/m^2. The curves have been shifted up on the vertical axis to aid in comparison. Both the T_g and the transition breadth for all the samples on the silica surface are increased compared to those in bulk as shown in **Table 2**. T_g increases in the order of 60 °C have been observed previously for ultrathin films of atactic PMMA on silica.[4] At 0.8 mg/m^2 the MDSC curves for the adsorbed polymers exhibit maxima between 170 °C and 180 °C. However, it is clear that the low molecular weight polymer has more intensity in the higher temperature region. As the adsorbed amount is increased to 1.8 mg/m^2, the curves shift to lower temperatures.

Since the glass transition temperature can be thought of as the temperature above which polymer chains exhibit significant segmental motion, an increase in T_g at a surface suggests that the polymer matrix is confined by the solid substrate. Using attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy, it has been verified that PMMA adsorbs on silica by hydrogen bonding between the PMMA carbonyl groups and the surface silanols.[5] These hydrogen bonds inhibit segmental motion. The broadened transition breadth is consistent with inhomogeneity in segmental motions and the different peaks can be attributed to the different fractions, each with their own T_g. The peaks at higher temperatures correspond to the more restricted fractions closer to the surface.

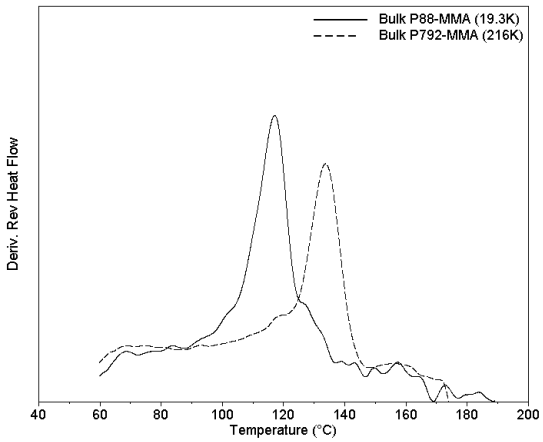

Figure 1. MDSC Curves for the bulk polymers.

The Scheutjens-Fleer (SF) theory[6] predicts a decrease in the bound fraction, the fraction of segments in contact with the surface, with increasing polymer molecular weight and adsorbed amount. A higher bound fraction corresponds to a flatter conformation, whereas a lower bound fraction is indicative of an adsorbed layer with long loops and tails. Adsorbed polymers with high bound fractions would then be expected to exhibit higher glass transition temperatures than those with lower bound fractions. The former would have more restricted segmental motion. As the adsorbed amount is increased from 0.8 mg/m^2 to 1.8 mg/m^2, the bound fraction decreased in accord with the SF theory. The number and/or size of loops and tails increased with adsorbed amount and, consequently, lower glass transition temperatures were observed.

Table 2. Glass Transition Behavior of the PMMA Samples

Sample	Transition onset temperature (°C)	Transition end temperature (°C)	Transition Breadth (°C)
Bulk P88-MMA	110	123	13
Bulk P792-MMA	128	138	10
P88-MMA-Si (0.8)	131	193	62
P792-MMA-Si (0.8)	132	193	61
P88-MMA-Si (1.8)	148	208	60
P792-MMA-Si(1.8)	145	202	57

These findings are consistent with previous studies on the segmental dynamics of bulk and adsorbed poly(methyl acrylate)-d_3 (PMA-d_3) by deuterium solid-state nuclear magnetic resonance (NMR) spectroscopy.[7,8] The

deuterated methyl group was used to demonstrate that the segmental mobility of the adsorbed PMA-d_3 was more restricted and heterogeneous compared to that of the bulk sample. The mobility decreased as the adsorbed amount decreased.[7] In addition, the observed behavior was consistent with an interface that was graded in terms of mobility. The regions of higher mobility (a small fraction) were associated with the air-polymer interface while that of more restricted mobility was assigned to the polymer-silica interface. We believe that the broadness of the thermal transitions observed here are indicative of the graded interface.

Finally, the results of this work are also consistent with, though as not obvious as, prior NMR studies on PMA-d_3.[8] These studies showed that at similar adsorbed amounts, very thin layers of PMA had lower glass transitions for higher molecular weight materials. This is opposite of the behavior of polymers in bulk. While not as dramatic, **Figure 2** illustrates this for the polymers at lower coverage (0.8 mg/m^2).

Conclusions

We have used modulated differential scanning calorimetry to study the glass transition behavior of PMMA thin films on silica. The glass transition temperatures of all the adsorbed polymers were higher than bulk. The surface glass transition temperatures increased with decreasing adsorbed amount. We suggest that the difference in the glass transition temperatures result from differences in chain configuration on the surface.

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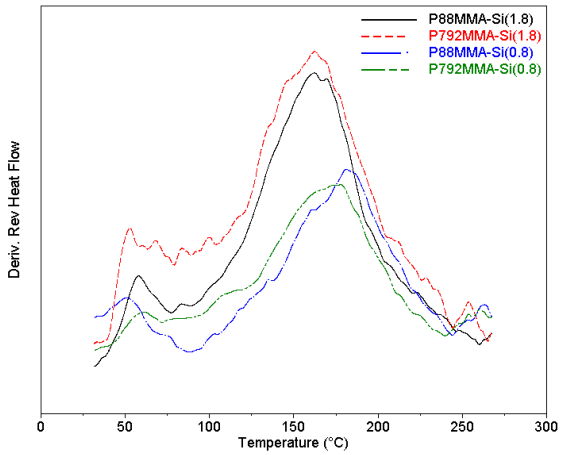

Figure 2. MDSC Curves for the adsorbed polymers at 0.8 and 1. 8mg/m^2.

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